

Study of Geometrical Parameters of Substituted Benzoquinones and Phenols by Density Functional Theory: A review

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Density functional theory is a quantum mechanical modeling method used to investigate the electronic structure of many body systems. In the present review different parameters of substituted benzoquinone compounds and phenol compounds are taken. FT-IR, FT-Raman spectra etc. of these compounds are recorded and the structural and spectroscopic data of these compounds in the ground state have been calculated by using Hartree-Fock and Density functional methods. On the basis of agreement between calculated and experimental results of the fundamental vibrational modes. I concluded that density functional theory gives good explanation.

Keyword: Density functional theory (DFT), FT-IR and FT-Raman spectra, Hartree Fock theory, Vibrational modes.

1. INTRODUCTION

In the past two decades quantum chemical computational methods have proven to be an essential tool for interpreting and predicting vibrational spectra [1,2]. In spectroscopy the absorbed radiation in a spectrum provides information the energy differences amongst various eigen states of a molecule in the transition [3]. Benzoquinones and its derivatives are currently finding increasing application for several reasons as used in pharmaceutical industry, tanning agent for leather industry, photographic chemicals and also used as a chemical intermediate a polymerization inhibitor and oxidizing agent. 2,4,6-Trinitrophenol is a well known explosive and aminophenols used in photographic, pharmaceutical and chemical dye industry etc. We have studied different geometrical parameters by using Hartree-Fock [4], Density functional methods and FT-IR, FT-Raman, X-ray etc. experimental methods.

2. LITERATURE SURVEY

2.1. Survey of different Parameters of Benzoquinone and their Substituents

2.1.1. Benzoquinone and Benzohydroquinone

Yuanzhi sang *et al.* [5] worked on Benzoquinones and Hydroquinone. Geometric parameters, the vibrational frequencies and thermochemical values of benzoquinone (BQ) and hydroquinone (BQH₂) were computed using ab initio molecular orbital

calculations (HF) and density function theory (B3LYP) method the 6-31 G(d) basis set respectively, which are tabulated in Table 1. Numbering of atoms is shown in Figure 1.

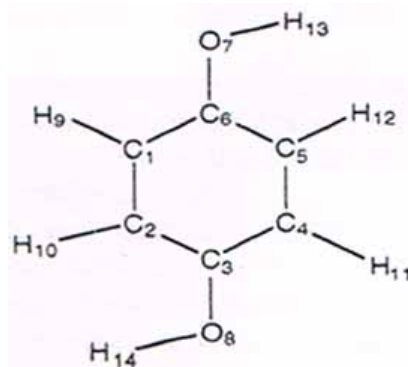


Fig. 1: Numbering in both BQH₂ and BQ

Table 1: Parameters of BQH₂ and BQ

Parameters	BQH ₂			BQ		
	B3LYP	HF	Exp.	B3LYP	HF	Exp.
Bond lengths (Å)						
C ₁ C ₂	1.397	1.384	1.390	1.372	1.323	1.344
C ₆ O ₇	1.373	1.358	1.377	1.266	1.194	1.224
Bond Angle (°)						
C ₆ C ₁ C ₂	120.1	120.2	120.0	122.7	121.4	121.0
C ₅ H ₆ O ₇	122.9	122.8	123.0	122.7	121.4	121.0

2.1.2. Aniline 1-4 benzquinone

Cludio H.B.Silva *et al.* [6] worked on Aniline 1-4 benzquinone. Assignments of FTIR and Raman bonds of AnBzq based on DFT results for An3Bzq1 model (wave number in cm⁻¹) are given in Table 2.

Table 2:

Experimental FTIR	Experimental Raman	DFT An3Bzq	Assignment
1674	1676 ^a	1634	$\gamma_{as}c = 0(bzq) + \gamma c = c$
1637	1633 ^a	1613	$\gamma_s c = 0(bzq) + \gamma c = c(bzq)$
-	1582 ^a	1575	$\gamma c = c(bzq) + \phi 8b$
-	1529	1515	$\beta N - H$
1505-1489	-	1514-1496	$\beta N - H$

a- Bands observed with higher relative intensities in spectrum at 568mm.

2.1.3. 2, 5 dihydroxy-1,4-benzoquinone

A. Sjabo, Akovacs [7] worked on 2, 5 dihydroxy-1,4-benzoquinone. Numbering of atoms is shown in Figure 2.

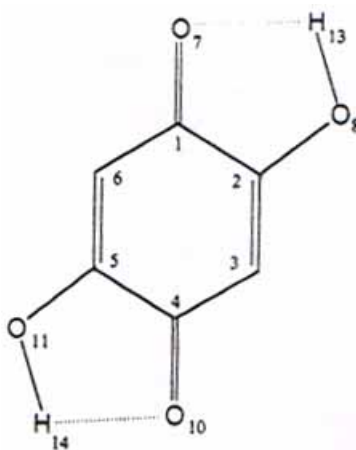


Fig. 2: 2, 5 dihydroxy-1,4-benzoquinone.

Geometrical and Fundamental parameters of 2, 5 dihydroxy1,4-benzoquinone are given in Table 3 and 4 respectively.

Table 3: Geometrical parameters of 2, 5 dihydroxy1,4-benzoquinone.

Parameter	B3LYP/6-3/G*	MP2/6-31+G**	X-Ray
C=C	1.357	1.359	1.355
C ₁ -C ₂	1.525	1.512	1.506
C=O	1.234	1.246	1.235
C ₁ -C ₂ -C ₃	122.9	122.6	122.0
C ₂ -C ₁ =O	115.3	116.3	117.2
O ₇H8	2.569	2.614	2.658

Distances are in angstrom and angles are in degrees.

Table 4: Fundamentals (cm⁻¹) of 2,5 dihydroxy 1, 4-benzoquinone.

ν	Experimental	Calculated		
		Unscaled	Scaled	Characterization (TED)
1	3290W	3406 (-)	3354	100% OH st
2	1630 s	1728(-)	1632	75% c=O st
3	657 ^d s	793 (197)	657	100% OH t
4	180 w	167 (1)	174	78% ringt, 12% c-o w, 10% C=O w
5	1664m	1706 (172)	1655	48% c=c str, 22% C=O str 13% c-c
6	428m	436 (30)	431	68% C.C=Ob 19% C-C str, 10% C=C st

TED - Total energy distribution

st, t, w - stretch, bend, wag respectively.

2.2. Survey of different Parameters of Substituted Phenol Molecules

2.2.1. 2,4,6 tri nitro phenol (T.N.P.)

Li Xiao Hong, Zhang Xian- Zhou [8] worked on 2, 4, 6 trinitro phenol. T.N.P. commonly known as picric acid is a non linear optical crystal used in dyeing industry [9]. It is well known explosives. Recently 2, 4, 6 – trinitrophenol has been reported by Srinivasan [10] which shows good crystallizability, high SHG efficiency and phase-matching character. Vibrational frequencies and geometrical parameters of the TNP molecule have evaluated by density functional theory (DFT) with 6-311++G** basis set, and compared with the

experimental vibrational frequencies which are shown in Table 5 and numbering of atoms is shown in Figure 3.

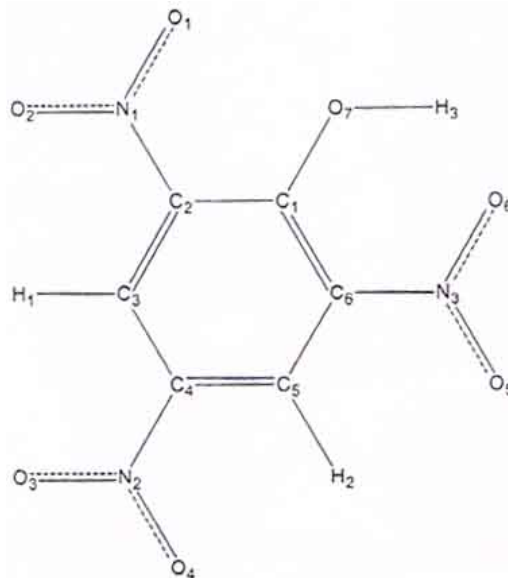


Fig. 3: Atom numbering in 2, 4, 6 tri nitro phenol.

Table 5: Calculated frequencies 2, 4, 6 trinitrophenol

	HF	B3LYP	Experimental (IR)	Assignments
1	541 (6.79, 0.76)	530 (1.32, 1.59)	521	$\delta(\text{ring})$
2	718 (10.88, 2.12)	697 (0.25, 1.38)	729	$\omega(\text{NO}_2) + \phi(\text{ring})$
3	734 (83.22, 0.32)	739 (75.90, 0.64)	832	$\delta(\text{O} - \text{H})_{\text{OOP}}$
4	3546 (445.24, 55.92)	3210 (446.07, 173.00)	3620	Intramolecular $\nu(\text{O} - \text{H})$

There is a good agreement between calculated and experimental parameters

2.2.2 Cis 3- amino phenol and Trans – 3 amono phenol

Y. Bugukmural, S. Akyuz. [11] Studied about cis 3-amiophenol (cis 3APL) and trans 3-aminophenol (trans – 3APL) Conformers.

Experimental and calculated (DFT) parameters are shown in Table 6 and Table 7. Numbering of atoms is shown in Figure 4.

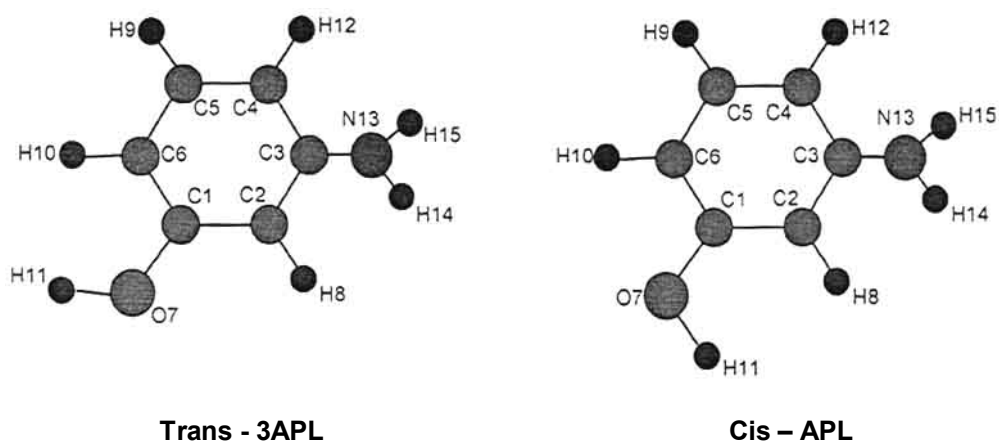


Fig. 4: Numbering of atoms.

Table 6: Cis – 3APL parameters

	Assignment	Phenol Exp.	Solid 3-APL		B3LYP/6-31++ G(d,p) scaled
			IR	Raman	
ν_1	CH stretching (γ_{OH})	3657	(3650) ^d	-	3665
ν_4	CH stretching (γ_{CH})	3087	3084	3081sh	3115
ν_8	NH ₂ Scissoring (δ_{NH_2})	-	1604	1601	1637
ν_{15}	CO stretching (γ_{co})	1262	1304	1314	1301
ν_{22}	Ring deformation (δ_{ccc})	823	963	963	953

Table 7: Trans– 3APL parameters.

Mode of Vibration	Assignment	Phenol Exp.	Solid 3-APL		B3LYP/6-31++ G(d,p) scaled
			IR	Raman	
ν_1	CH stretching (γ_{OH})	3657	3650	-	3667
ν_4	CH stretching (γ_{CH})	3087	3084	3081sh	3071
ν_8	NH ₂ Scissoring (δ_{NH_2})	-	1604	1601	1626
ν_{15}	CO stretching (γ_{co})	1262	1304	1314	1311
ν_{22}	Ring deformation (δ_{ccc})	823	963	963	953

A comparison of the vibrational analysis of 3 APL experimental and theoretical study gave a full – description of the geometry and based on calculated energy differences, the trans - conformer is found to be more stable than the cis - conformer [11].

4. CONCLUSION

Here experimental and theoretical vibrational analysis of the investigated molecules gave us a full description of the geometry, harmonic frequencies and vibrational properties of the investigated compounds. The investigated molecules are analyzed by ab –intio, HF and DFT (B3LYP).

The calculated vibrational frequencies obtained with density functional theory are in good agreement with experimental values obtained for investigated compounds. The study demonstrates that DFT / B3LYP calculation are powerful approach for understanding the vibrational spectra of investigated compounds.

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